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O. V. Kylosova, A. B. Ilbuldina, O. V. Yaroslavtseva
Ural Federal University, 19 Mira street, 620002 Ekaterinburg
E-mail: o. v.yaroslavceva@urfu.ru

Study of instantaneous rate of corrosion of aluminum in media with different acidity

Instantaneous rate of aluminum corrosion in media with different acidity has been studied using a method of polarization and the electrical resistance. A resulting time series of instantaneous corrosion rate have been analyzed using the standardized range. As a result, it has been found that in all studied media corrosion process has a stochastic character, and time series of instantaneous rate are anti-persistent.

Key words: electrochemistry, corrosion, aluminum.

Introduction

From the viewpoint of observation of the development of corrosion process of greater interest is the differential characteristic of the rate of corrosion, so-called instantaneous rate of corrosion [1].

Since the corrosion process on the metal surface is likely to develop very unevenly, so fixing the instantaneous values of the corrosion rate one can be trace the alternation of its activation followed by temporary decay, which could again be replaced by reactivation. Observations of such changes in instantaneous rate at the initial stage of the corrosion process development can be used as the basis for the development of long-term corrosion forecast model. Therefore the choice of methodology of instantaneous corrosion rate research is actual.

Experimental part

As an object of the study aluminum wire (Al not less than 99.6–99.7 % (wt.)) has been used.

The instantaneous rate of corrosion of aluminum has been studied in three solutions: H_2SO_4, Na_2SO_4 and NaOH, a pH of which was 0.78, 5.71 and 11.11 respectively. The instantaneous rate of corrosion has been evaluated by two methods: polarization and electrical resistances. Measurement of polarization resistance and recording polarization curves have been performed in a standard electrochemical cell with divided cathode and anode spaces using Solartron 1280 C test station. A measurement design is shown in Fig. 1.

A program of measurement of the polarization resistance has included

300 cycles, which consisted of measuring the currentless potential for 10 seconds, followed by potential sweep from –15 to +15 mV relative to the stationary potential, sweep rate is 3 mV/s. Polarization curves for determining Tafel coefficients have been recorded by polarization from the cathode region to the anode one at linear potential sweep of 3 mV/s.

Measurement of electrical resistance has been carried out by means of high-resistance voltmeter. A measurement design is shown in Fig. 2. The time interval between measurements was 30 seconds, in each solution up to 300 measurements have been performed.

Results and Discussion

A typical curve of the time dependence of the experimental polarization resistance of the aluminum sample is shown in Fig. 3.

According to experimental data of the polarization resistance (R_p) values of instantaneous corrosion rate in current units (i_{korr}, А/см^2) have been calculated by the Stern-Geary equation [2]:

$$i_{korr} = \frac{b_a \cdot b_k}{2{,}3 \cdot (b_a + b_k) \cdot R_p}, \qquad (1)$$

wherein b_a and b_k are the Tafel slopes of the anodic and cathodic processes.

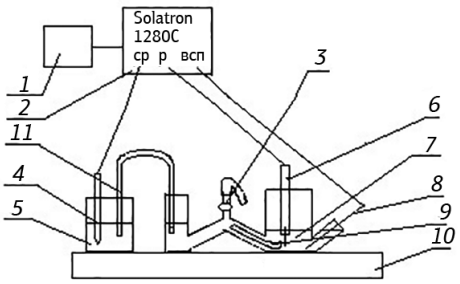

Fig. 1. Apparatus for polarization measurements: 1 – computer; 2 – electrochemical station; 3–3-way stopcock; 4 – silver chloride reference electrode; 5 – saturated solution of KCl; 6 – working electrode; 7 – working solution; 8 – platinum auxiliary electrode; 9 – Haber-Luggin capillary; 10 – support for the cell; 11 – salt bridge

In all solutions under study oscillations have presented on the time dependence of the instantaneous corrosion rate. The presence of oscillations proves that the corrosion process has a stochastic character. The amplitude of oscillations and the general trend of change of polarization resistance suggest the following features of the corrosion process:

– in a neutral salt solution dissolving aluminum occurs in pores existing on the surface of the oxide film;

– in sulfuric acid solution the initial more or less active dissolution is replaced by the reduction of the oxide film, and the dissolution process slows down and localizes in pores of the oxide film;

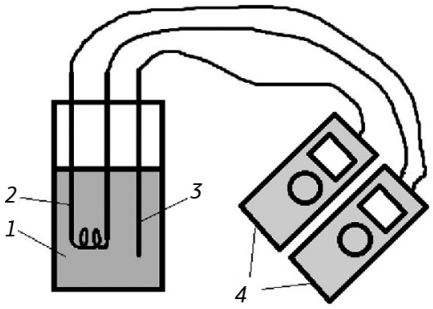

Fig. 2. The electric resistance measuring circuit 1 – glass with the test solution, 2 – sample (in the form of wire spiral), 3 – thermocouple, 4 – high-resistance voltmeters

– in alkali medium dissolution of aluminum observed in cracks of fast-growing aluminate film.

Experimental curves of the change in time of the aluminum sample electrical resistance also had characteristic oscillations in all studied media (Fig. 4).

The instantaneous rate of corrosion (V, μm/s) can be calculated from the dependence of the electrical resistance on the radius of the wire sample [3]:

$$V = -\frac{\partial r}{\partial t} = \left(\frac{\rho \cdot l}{4\pi}\right)^{1/2} \cdot R(t)^{-3/2} \cdot \frac{\partial R}{\partial t}, \qquad (2)$$

wherein r is the radius of aluminum wire; ρ is the electrical resistivity of aluminum; l is the length of aluminum wire; $R(t)$ is the resistance value at time t.

The resulting time dependencies of the corrosion rate have oscillations regardless of the composition of the corrosive solution. This indicates that despite the significantly different values of the electric resistance and oscillation amplitude in different solutions the stochastic character of dissolution maintains.

In order to identify the character (random or fractal) the time series have been processed by the method of Hurst. The method involves the standardization of data to zero, mean and standard deviation. The calculated values of the Hurst exponent for the time series of polarization and electrical resistances in the studied media (Table 1) are in the range from 0 to 0.5. Accordingly, all of the analyzed experimental time series are anti-persistent, so observed at the initial time moment the growth of corrosion rate subsequently may give place to a decrease.

Table 1

The Hurst exponent for the time series of polarization and electrical resistance

Time series	Solution		
	H_2SO_4	Na_2SO_4	NaOH
Polarization resistance	0.42 ± 0.21	0.27 ± 0.13	0.27 ± 0.08
Electrical resistance	0.29 ± 0.02	0.29 ± 0.05	0.33 ± 0.04

Conclusion

1. Studies of electrochemical behavior of aluminum by electrical and polarization resistance in solutions with different pH have been carried out.

2. On the basis of the obtained time dependencies of the instantaneous corrosion rate it was confirmed that the process of corrosion on the surface of

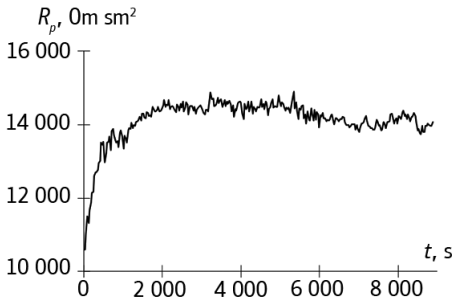

Fig. 3. The polarization resistance of the aluminum sample in sodium sulfate solution

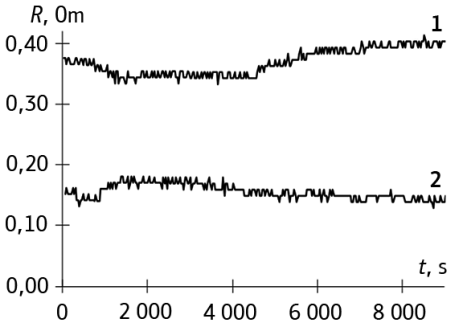

Fig. 4. The electric resistance of the aluminum sample:
1 – in sulfuric acid; 2 – in alkali medium

the aluminum sample develops non-monotonically: oscillations presented on graphs suggest the stochastic character of the process.

3. When processing time series of polarization and electrical resistance it was revealed that the corrosion process on the aluminum surface has anti-persistent character regardless of the presence of the passive film.

The results of the measurement of the polarization resistance data have confirmed known data on aluminum corrosion resistance in media with different pH, more specifically:

– destruction of the passive film and intensive dissolution in alkaline solution;

– passivation of the oxide film in a neutral solution;

– reduction by the present in the solution oxygen of the oxide film dissolving upon contact with an acidic solution.

5. The analysis of experimental data has revealed that the corrosion rate determination by the electric resistance is possible in case of active dissolution of the metal in a corrosive medium, for example aluminum in an alkaline medium. In the presence of the growing passive film this method is not applicable.

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